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Correlation between structural and optical properties of nanocrystal particles prepared at low temperature plasma-enhanced chemical vapor deposition

D. Milovzorov†‡§, T. Inokuma†, Y. Kurata† and S. Hasegawa†
† Department of Electronics, Faculty of Technology, Kanazawa University, 2-40-20 Kodatsuno, Kanazawa 920, Japan
‡ Institute of Radioengineering and Electronics, Russian Academy of Science, Mokhovaya str. 11, Moscow 103907, Russia
§ Present address: The Institute of Physical and Chemical Research (RIKEN) Wako, Saitama 351-01, Japan

In recent years a great interest has been generated in formation of semiconductor with nanocrystals, due to their unique properties resulting from quantum confinement in systems of reduced dimensions [1, 2]. For these materials there is a potential for fabricating optoelectronic devices and optical amplifiers.

Polycrystalline silicon (poly-Si) film synthesis has been deposited on quartz, glass (Corning 7059) and Si (100) substrates by low temperature plasma-enhanced chemical vapor deposition (PECVD)using SiH_4/H_2 and $SiF_4/SiH_4/H_2$ gas mixtures. The substrates were cleaned for 20 min, by nitrogen and hydrogen plasma respectively, just before the deposition of poly-Si films. The rf power supply was 20 W (at 13.56 MHz). The SiH_4 flow rate was maintained at 0.6 sccm. The hydrogen flow rate was varied from 5 to 46 sccm. Using a SiF_4 gas diluted with He (He: 95%, SiF_4: 5%) the SiF_4 was varied from 0 to 0.5 sccm. The total gas pressure was 0.2 or 0.3 Torr.

The structural properties of the poly-Si films were investigated by means of x-ray diffraction (SHIMADZU XD-D1) employing a diffractometer with the slit width 0.1 mm, set in the front of the detector. The XRD relative intensity was defined as the integrated area including the following corrections; the difference in film thickness for each sample was corrected using the x-ray absorption coefficient for Si, and the XRD intensity of a given texture was further normalized using corresponding x-ray intensities for Si powder. The average grain size, δ, in the depth direction was estimated from the half-width value of the x-ray spectrum by means of the Scherrer formula [3].

The volume fraction of crystalline phase, ρ, was estimated from the intensity of Raman spectra by the procedure proposed by Tsu et al [4], that is, a Raman spectra consists of two components: crystalline Si (c-Si) phase corresponds the spectral peak near 520 cm^{-1} and amorphous Si (a-Si) phase at around 480 cm^{-1}. The ρ values were estimated from the intensity ratio of the above two components using the ratio of the integrated Raman cross section for crystalline and amorphous phases. The crystalline volume fraction for the films used was between 60% and 80%.

Photoluminescence (PL) was analysed using a Jobin Yvon RAMANOR HG 2S spectrometer coupled with a cooled photomultiplier tube (Hamamatsu Photonics K.K.). The 488 nm Ar^+ laser line with power ranging from 300 to 500 mW was used as the PL excitation source.

The chemical structure for the surface region on crystallites was investigated by

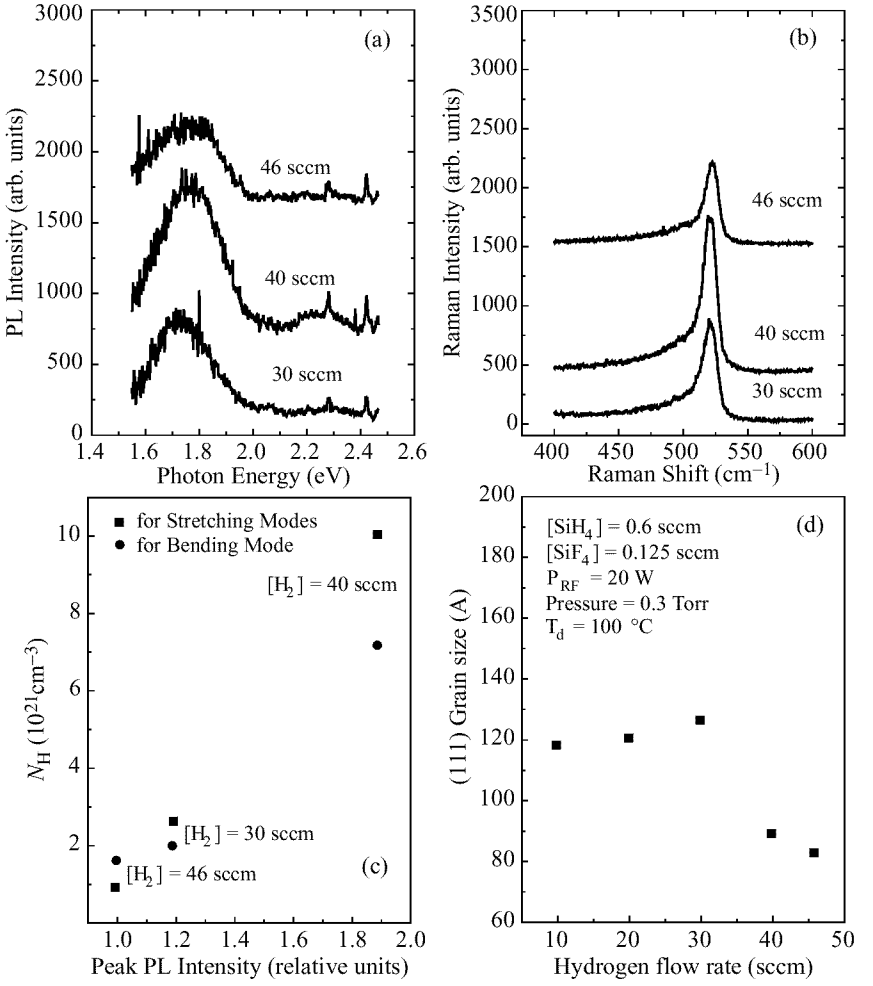

Fig 1.

means of Fourier-transformed infrared spectrometer (JASCO FT/IR-610). The density of given bonds can be estimated by the following way:

$$N^{v}_{\mathrm{SiM}} = A^{v}_{\mathrm{SiM}} I^{v}_{\mathrm{SiM}}, \qquad (\mathrm{M} = \mathrm{H\ or\ O})$$

where A^{v}_{SiM} is proportionality coefficient, I^{v}_{SiM} is the intensity of the SiM absorption spectrum with the given frequency v.

Using low temperature PECVD of $SiF_4/SiH_4/H_2$ gas mixture we produced the poly-Si films which contains hydrogenated nanocrystallites with different luminescent properties. Figure 1(a,b,c,d) illustrates the relationship between PL spectra, Raman spectra, density of bonds for hydrogen stretching and bending modes, and average grain size as function of hydrogen flow rate, respectively. The temperature of deposition was 100°C.

The PL peak energy of hydrogenated nanocrystals is sensitive to the deposition conditions. Figure 2 shows the increase of PL energy as function of average grain size under

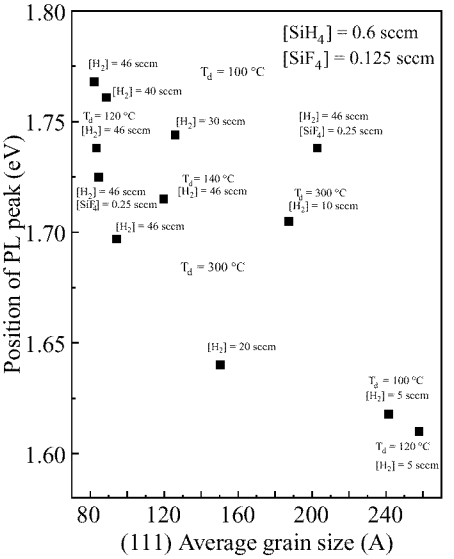

Fig. 2.

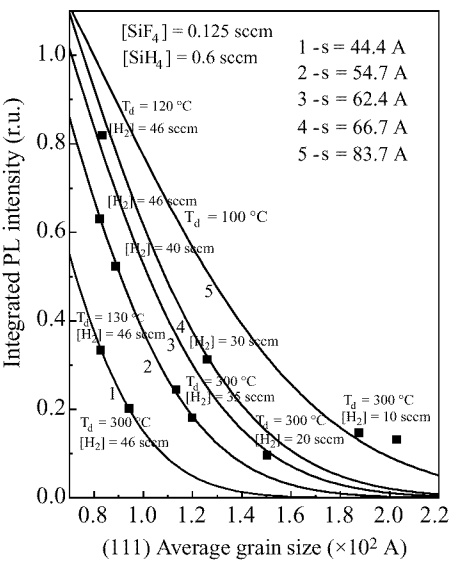

Fig. 3.

different PECVD conditions. Each point in this results illustrates the correlation between the PL peak energy and average value of grain size. PL peak energy corresponds the energy band gap of crystallites and is result of the presence the small nanoparticles in left tail of size distribution. We can see that highest points in Fig. 2 are realized with low temperature (100°C) conditions. It is connected with wider size distributions with strong long left tail which contain a great amount of nanocrystallites. The increase in the deposition temperature causes the decrease of the PL peak energy. In this case, the band gap energy of the crystalline core state is lower than the ~ 1.65 eV interface state [5]. The size-dependent PL characteristics in hydrogenated nanocrystals is result in presence delocalized states in the Si crystalline core. It is obvious that as the crystallite size decreases the highest occupied state energy decreases and the lowest unoccupied state energy increases. By changing preparation conditions of deposition such as deposition temperature, hydrogen or SiF_4 flow rates there is adjustable the size distribution of crystallites and their hydrogenation. The presence of dangling bonds would suppress the PL response. The termination of dangling bonds with hydrogen removes localized defect states from the energy range near the Fermi energy in the surface region on crystallites.

Figure 3 shows the integrated PL intensity as function of average grain size. The calculated curves for the PL intensity were obtained by assuming the state-to-state spontaneous transition probability and absorption coefficient [6]. Our PL response model involves absorption in the quantum confined Si cores, and emission due to transitions between states in terminated layers. The results of calculation according to the model are presented by solid lines in Fig. 3. In these calculated curves, the size dependence of the integrated PL intensity can be expressed in the following form: $I \sim \rho \exp(-\delta k/2)$ where ρ is proportional constant, and $k = 1/\sigma^2$; σ is standard deviation. The values of the standard deviation estimated from solid lines in Fig. 3 changed from $\sigma = 44.4$ Å

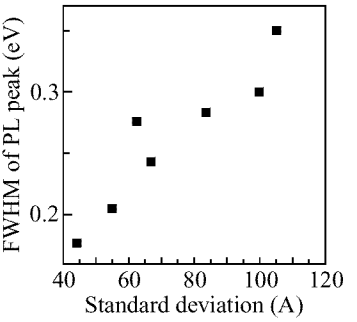

Fig 4.

(curve 1) to σ = 83.7 Å (curve 5). We find a tendency that the standard deviation becomes larger as the deposition temperature decreases. However, at low temperature, highly efficient PL can not be found. This may be because high integrated PL intensity of films deposited at low temperature is realized due to the great spectral width. As a consequence, for high performance of the material the use of higher deposition temperature (200–300°C) and high hydrogen dilution ratio is more preferable, because the film which has small σ value, which has a relatively small σ value, will result in the PL response with narrow width of energy. Figure 4 shows the correlation between the width of PL spectra and value of σ (which is estimated from different curves in Fig. 3). As seen in Fig. 4, the width of PL spectra decreases with decreasing σ values. Therefore, we can suppose that spectral width of PL is proportional to the standard deviation of size distribution of crystals.

In conclusion, we have synthesized poly-Si films with controlled size distribution of nanocrystals and sufficient luminescent properties. The correlation between structural and optical properties of the poly-Si films allows us to determine the optimal deposition conditions for preparation films with high PL response with narrow width of energy.

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